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Final Report
to the

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"PARAMAGNETIC RELAXATION AT VERY LOW TEMPERATURES"

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Department of Physics
Michigan State University
East Lansing, Michigan

572 400

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The objective of the present research was an investigation of paramagnetic relaxation at low temperatures. In the original proposal and a subsequent renewal we listed the following situations in which we hoped to examine paramagnetic relaxation:

- (1) a) Nuclear relaxation as a function of paramagnetic centers;
- b) Antiferromagnetic relaxation examined by a probe nucleus or antiferromagnetic center;
- c) Second sound generation by relaxation energy;
- d) Paramagnetic relaxation in color centers and centers produced by irradiation;
- e) Paramagnetic relaxation at low fields and low frequencies.

Work was carried out in all these fields. In several cases the experiments were quite successful, in others they failed miserably and in still others they are incomplete. The general objective of an investigation of paramagnetic relaxation was certainly achieved. In the following paragraphs we summarize the published results with introductory and interpretive comments, and we review certain results which we have considered too preliminary to warrant publication but which suggest future directions for work.

In nuclear magnetic resonance, nuclei are raised to excited zeeman states by the absorption of energy from an applied radio frequency field. To return to their ground state the nuclei must release their energy to the liquid or crystalline media in which they are imbedded. The processes by which such an energy transfer can be accomplished are varied but the most important ones are certainly through couplings between nuclei and between nuclei and electrons. In the case of liquids both mechanisms are often operative while in solids only the nucleus-electron coupling is of much importance. The effectiveness of paramagnetic ions in providing a relaxation path between the nuclei and the lattice was recognized and demonstrated experimentally several years ago by Bloembergen. It follows that if we irradiate the paramagnetic electron system with microwave energy of sufficient intensity to saturate the levels of the electron system we may block the path by which the nuclei relax to the lattice. Experimentally we find this to be true provided the microwave frequency is precisely that corresponding to the splitting of the selection levels. If the microwave frequency is just slightly too large or too small a much more complicated

effect is observed in which the nucleus and the electron effectively couple together and act as a single unit as far as absorption of microwave energy is concerned. If the microwave photon has less energy than that required to bring the electrons to resonance, the electrons borrow energy from the nuclei with the result that the nuclei fall to lower levels and the effective nuclear temperature decreases. If the energy in the microwave photon exceeds that required for resonance the excess energy passes to the nuclei with the result that the higher nuclear zeeman levels become highly populated. With sufficient microwave power the population of the nuclear levels can actually be inverted corresponding to a negative absolute temperature for the nuclear system. The population of the nuclear levels in either of the two cases can easily be checked by measuring the intensities of the nuclear magnetic resonance lines while applying the microwave power. If the lower nuclear levels have a population in excess of that corresponding to the lattice temperature, the nuclear resonance signal will be enhanced. If, however, the population is inverted the nuclear resonance signal will appear as an emission signal rather than the customary absorption signal.

The material used in our experiment¹ was pink ruby - Al_2O_3 plus a small amount of chromium as the paramagnetic ion. The Al^{27} nuclear resonance was used to observe the effects indicated above. Both emission and enhanced absorption signals were observed. The enhanced signals at 4.2°K and at the microwave power then available to us amounted to about 30 times that observed without microwave power. Later experiments with higher microwave power and lower temperatures showed that one can achieve signal enhancements the order of several hundred. If the microwave power is switched on, the polarization effects build up in a time the order of seconds. In a second paper² we explore the way in which the magnitude of the signal enhancement and polarization time depends on the concentration of paramagnetic ions. Enhancements and polarization times were measured in ruby samples containing 0.01%, 0.1% and 0.25% chromium. In the 0.01% and 0.1% samples the enhancement was approximately 30 while in the 0.25% sample the enhancement was very small. The time constant for the build up or decay of the enhanced signal was 26 sec for the 0.01% samples, 2.6 sec for the 0.1% sample and less than one second in the .25% sample. The nuclear polarization effects were observed using both the steady state and the pulsed nuclear resonance technique. The dependence of the build up or decay time on the concentration implies that it measures the time for energy to diffuse through the lattice from one nucleus to another until a paramagnetic ion is finally reached. The ultimate enhancement appears to be limited by the rate at which the paramagnetic ion transfers energy to

the lattice by spin orbit coupling.

The experiment has found some interesting applications in other laboratories. It is currently being examined as a method for reaching low temperatures, achieving polarized proton targets for the cyclotron, improving the operation of the ruby maser and studying the nuclear resonance spectrum of rare species in a crystal. The general method seems likely to be an important tool in studying electron-nuclear interactions.

The electron-nuclear relaxation process is particularly difficult to study in magnetically concentrated systems because we do not have as yet any suitable mathematical model to describe the spectrum of the magnetic field which the fluctuating moments of the paramagnetic ions lay down at the nuclear sites. If the amplitude of the frequency components corresponding to splitting of the nuclear zeeman levels were known it would (in principle) be a straightforward problem to calculate the nuclear relaxation time. In the case of ferromagnets or antiferromagnets at temperatures well below their Curie or Neel temperature the spin wave theory enables one to predict a spectrum of magnetic field fluctuations and in these special cases one can derive theoretical expression for the nuclear relaxation time. The studies of Hardeman et al. of the proton spin lattice relaxation time in antiferromagnetic $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ reveal discrepancies between the theoretical and observed temperature dependence of this quantity. They find that the relaxation time varies as the inverse eighth power of the temperature while the theoretical calculations of Van Kranendonk and Bloom predict an inverse cube temperature dependence. They also find that the sublattice magnetization difference $M(0) - M(T)$ varies as T^4 while the theoretical results of Kubo et al. give at T^2 dependence.

The compound $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ which is antiferromagnetic below 4.5°K offers an opportunity to study the temperature dependence in a crystal with the same magnetic ion, essentially the same Neel temperature but quite different crystal structure. The space group of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is Pbnm while that of $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ is $\text{P2}_1/\text{C}$. In $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ we found³ that the relaxation time varied as the inverse fourth power of the temperature while the magnetization difference varied as the cube of the temperature. Thus while our results still show departures from the predictions of spin wave theory the differences are considerably smaller than in the case of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. Our results also suggest that the temperature dependence of these quantities is extremely structure sensitive. Recent theoretical attempts by Kittel to explain the difference between theory and experiment have invoked a coupling between spin waves and phonons.

In the process of examining the relaxation and magnetization

in $\text{LiCuCl}_2 \cdot 2\text{H}_2\text{O}$ we examined the nuclear resonance spectrum in some detail. ²Since it is a relatively new antiferromagnetic we attempted to obtain information about the antiferromagnetic spin arrangement in these crystals⁴. The local fields at both the proton and lithium sites were determined by examining the gross displacements of the resonance lines from the frequencies at which they would occur in a non-magnetic crystal. Fine structure is observed which arises from the dipole-dipole interaction for protons in the water molecules and the quadrupole interaction of the lithium nucleus. The fine structure studies made it possible to associate pairs of local fields with certain water molecules. By applying group theoretical methods to our results we were able to show that the antiferromagnetic spin arrangements must be one of three definite configurations. The fact that one can not be more definite than this arises from the fact that the crystal structure and magnetic susceptibility data on this crystal are not very complete and the location of proton and lithium sites is not known.

With a view to future work in the field of antiferromagnetism we turned to an examination of the problem of locating protons in crystals by nuclear magnetic resonance. Protons have previously been located by nuclear magnetic resonance in a number of simple crystalline hydrates for which the x-ray structure was known. To test the practicality of the nuclear magnetic resonance technique when applied to more complicated hydrates we studied⁵ sodium thiosulfate pentahydrate which contains 20 protons, in the unit cells. Using a modification of conventional techniques to unscramble the overlapping lines we were able to locate all the 20 protons. It is interesting to note that the protons occupy positions which are completely consistent with the hydrogen bonding scheme which has been proposed for this crystal. We feel that our results demonstrate the utility of the n.m.r. method in determining proton positions in crystals whose structure is otherwise known. Because of their small x-ray cross section proton positions are very difficult to determine by conventional x-ray methods. Their position can of course be determined by neutron diffraction but the process is certainly much more time consuming.

We next applied these methods to $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ⁵ which is a member of an isostructural series of antiferromagnets in which we have been interested for some time. Although the workers who had done the original x-ray study had been unable to postulate a satisfactory hydrogen bonding scheme, our method worked in a satisfactory manner and we were able to locate all the protons to a fair degree of accuracy. These results are now being used as a basis for the study of the series

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$ which are antiferromagnetic in the liquid helium temperature range.

In a discussion at the Kyoto conference on magnetism Spence and Poulis (Leiden) noted that both laboratories had found that in the mineral azurite the antiferromagnetic and paramagnetic phase can exist simultaneously in a temperature range of about 0.2°K . This result is remarkable in that the antiferromagnetic-paramagnetic transition is supposed to be of the second order and therefore admits of no superheating or supercooling. The Leiden group suggested that the peculiar results in azurite might be due to strains in the crystal or to short range ordering effects. The specific heat studies of Forstater⁷ have shown that the $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ shows even more short range order near the Neel temperature than azurite. We therefore decided to examine $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ for evidence of coexistence of the two phases. We found⁸ that the two phases do indeed overlap but only over a range of about 0.02°K which appears to show that the short range order is not the primary cause of this phenomena. Since the time of our original work a number of other laboratories have obtained results indicating the coexistence of phases in other antiferromagnetic crystals.

The studies of the relaxation time in $\text{LiCuCl}_3 \cdot 2\text{H}_2\text{O}$ were, done in both an applied field and in zero field. In the process of making these studies we found that it was possible to determine not only the magnitude but also the direction of the local fields in antiferromagnets. The technique has the advantage that it is much faster and much less apt to perturb the spin arrangements than the conventional applied field technique. The new technique is currently being used to study a number of antiferromagnetic crystals and will be reported in part of a forthcoming paper.

In the process of testing our relaxation time apparatus we examined an interesting organic complex¹⁰. Mixtures of phenyl isothiocyanate and diethylamine show a sharp maxima in the viscosity at equimolecular proportions rising to a value 26,000 times that of its most viscous component. The values of the relaxation time as a function of concentration clearly reflected the viscosity maximum at 50 mole %. However attempts to fit the data with conventional relations between viscosity and relaxation time failed. The mixture is a complicated system which appears to form a new compound at each concentration.

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R. Vieth

H. VanTill

G. H. Khan

P. Middents

C. R. K. Murty

W. R. Schafer

E. S. Gravlin